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Properties of Diamond Composite
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PROPERTIES OF DIAMOND COMPOSITE FILMS GROWN ON IRON SURFACES

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ABSTRACT

We report for the first time that diamond composite films consisting of diamond particles, hydrogenated amorphous carbon and/or fluorocarbon films can be successfully deposited on carbon steel and 304 stainless steel substrates by plasma assisted chemical vapor deposition. The use of thin (~ 200 Å) silicon buffer layer proves to be effective in inhibiting surface catalytic effect of iron and also prevents carbon species from diffusing into the bulk. The composite films adhere well to the substrates even upon imposing a scratch load of 68 newtons. They can also be bent up to ten degrees and still remain chemically inert and impermeable to salt solutions. One of the potential application of these films is for protective coating on sheet metal surfaces.

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Research on diamond thin films has captured worldwide interests¹⁻³ ever since W.G. Eversole discovered⁴ a process of synthesizing diamond from hydrocarbon gas precursors. Its high strength and chemical inertness make diamond film a good protective coating material. However, there are still unresolved issues regarding the nucleation and growth of these films. For examples, the coefficient of thermal expansion mismatch between the films and substrates such as iron, alumina, molybdenum etc. will result in poor adhesion property. In addition, it is extremely difficult to nucleate diamond particles on iron, cobalt, or nickel based materials due to the catalytic effects of these elements on gas precursors such as methane to form soot⁵. Moreover, the rapid diffusion of carbon species into the iron based metals, such as carbon steel and stainless steel, consumes a significant portion of carbon species on the substrate surface for diamond growth.

In this letter, we introduce for the first time : 1) a novel process for depositing diamond composite films consisting of diamond crystallites covered by a layer of hydrogenated amorphous carbon (a-C:H) and/or fluorocarbon polymer , 2) the use of a thin buffer layer (such as amorphous silicon) to inhibit surface catalytic effect and as a diffusion barrier for carbon species. The composite films have the following properties : good adhesion, hardness, wear resistant, corrosion resistant, chemically inert, and flexible. The diamond particles in the composite function as strength/hardness reinforcement for the composite structure. The a-C:H and fluorocarbon films are used because they are relatively flexible compared to diamond. Furthermore, the a-C:H films have been known to have the unique diamond-like properties, as well as the unusual smoothness and pinhole free microstructure^{6,7}. Fluorocarbon polymer films have been known to possess some outstanding properties as well⁸. These unique and flexible films have potential applications for coating on sheet metals and aircraft wings. This is in contrast to pure diamond films which are very stiff and inflexible.

In our experiment, a 2.45 GHz microwave plasma chemical vapor deposition (CVD) apparatus⁹ is used to deposit diamond particles. Clean mirror-polished carbon steel and 304 stainless steel substrates are used in our experiments. The substrates are first rubbed with 1/4 μm diamond powder on a soft polishing cloth, and then ultrasonically cleaned with acetone and methanol for approximately 10 minutes. The substrates are then coated with $\sim 200 \text{ \AA}$ of amorphous silicon (a-Si) which is prepared by conventional thermal evaporation technique. The thickness of this buffer layer has been empirically optimized for nucleation of diamond. There are

two factors that govern this optimization: the plasma environment and the substrate temperature. In our plasma for diamond nucleation and growth, there is a combination of sputtering, etching and deposition taking place on the surface of the substrate. If an iron substrate surface is covered with too thin a layer of a-Si, then a combination of sputtering and hydrogen etching will completely remove it away before diamond particles can nucleate appreciably and grow. Because our substrate is inductively heated by the incident microwave, the substrate temperature increases in time initially. If the barrier layer is too thick, then the carbon precursor species will not find the nucleation sites on the iron surface prepared by diamond powder polishing during the initial temperature rise of the substrate. It is during this initial temperature rise that most of the nucleation takes place. Even though the hydrogen etching of the silicon barrier takes place at all substrate temperature, at high ($> 600^{\circ}\text{C}$) substrate temperatures the silicon layer will start to oxidize due to the presence of the oxygen in the plasma. Once the oxide layer is formed, the hydrogen etch rate is dropped by about an order of magnitude¹⁰. This oxide layer quenches the thickness reduction process of the barrier layer for nucleation of the diamond on the iron surface.

Precursor gases are introduced into the system at the very initial stage when the plasma is just turned on. Diamond nucleation is enhanced using this technique since the average substrate temperature is low at the beginning¹¹. Typical deposition conditions are : gas mixture, CH₄ : H₂ : O₂ = 1 : 99 : 0.4 ; total flow rate = 100 sccm ; pressure = 40 mbar ; microwave power = 280 W. Hydrogenated a-C and fluorocarbon polymer films are deposited using a parallel plate, capacitively coupled rf plasma system. The substrates are placed on the powered, negatively self biased, electrode (cathode) for the case of depositing a-C:H layer, allowing the positive ion bombardment action to take place on the substrate surface during the film growth. The deposition of fluorocarbon film is carried out by placing the substrate on the anode. Table I lists the deposition conditions for both carbon films.

Scanning electron microscopy (SEM) is used to study the morphology of the diamond particles. The results reveal the typical cubooctahedral facets of the crystals (2000-4000 Å size) and the five fold twinnings¹², as clearly shown in Figure 1. No preferred orientation of the crystals is observed. Nucleation density in terms of surface area is designed to be approximately 50-75 % of the total substrate surface. Figure 2 depicts a cross sectional view of the diamond and

approximately 4000 Å thick a-C:H composite film on carbon steel substrate. The resulting composite films are smooth within a few hundred angstroms and uniform in thickness.

A three-point bending tester is used to evaluate the flexibility of the composite films. The specimen is subjected to continuously increasing loads with cross head speed moving at 200 $\mu\text{m}/\text{min}$. The sample dimension is : thickness = 0.60 - 0.66 mm; width = 6.00 - 6.60 mm ; length = 10 mm. Figure 3 shows the load (which has been normalized with respect to the width and the thickness of the specimen) versus vertical displacement (δ) data for sample : (a) bare 304 stainless steel ; (b) a-C:H film, fluorocarbon film, and diamond particles on 304 stainless steel ; (c) a-C:H film and diamond particles on 304 stainless steel ; (d) fluorocarbon films and diamond particles on 304 stainless steels. Unlike sample (d), sample (b) and sample (c) experience film cracking at the very early stage of plastic deformation, as indicated by the black arrow markers which depict a sudden stress relaxation. These correspond to the critical sample displacements (δ_c) equal to 0.42 mm for sample (b) and sample (c), and 0.56 mm for sample (d). From the results of sample (d), it was expected that the fluorocarbon interlayer in sample (b) would experience cracking at δ_c somewhere intermediate between sample (c) and sample (d), and provide the extra protection in case of cracking failure of the top layer (a-C:H film). However, the fluorocarbon and the top a-C:H layer in sample (b) crack simultaneously. Hence, no improvement in the bendability of the film can be obtained. The reason is that there is good adhesion of the fluorocarbon film to the substrate and the top a-C:H film. As a result, the fluorocarbon interlayer is experiencing the strong adhesive forces upon bending the sample not only at the interface with the substrate, but also at the interface with the a-C:H layer. The critical bending angles corresponding to the precracking condition have been evaluated to be 10 degrees for sample (b) and (c), and 13 degrees for sample (d). As a comparison, Gille and Wetzig¹³ reported the δ_c values for the commonly used TiC and TiN coatings on C100W1 and X82WMo6.5 steels based on four-point bending tests. The equivalent bending angle values range from two to four degrees. Their results are clearly inferior to our findings obtained by three-point bending which is known to be a more severe test.

The composite coatings (samples (b), (c), and (d) of Figure 3) have been subjected to variety of chemical tests (i.e. 3 HNO₃+7HCl+20H₂O, 48% HF, 96% H₂SO₄, 37% HCl, 71% HNO₃, 5g NaCl+100 cc H₂O, CCl₄, and CHCl₃) to evaluate their chemical resistance and permeability

before and after the bending tests. The salt solution test is performed only on the coated steel substrates by immersing the sample for approximately four hours. For other chemical tests, a drop of the solutions is placed on top of the coating for several minutes. The results, as examined using optical microscope, show that the films are inert to all of the chemicals and impermeable to the salt solution. However, upon film cracking, all of the samples, including sample (d) of Figure 3 fail all of the acid and salt solutions tests due to reaction at the film and substrate interface by the chemicals penetrating through the crack openings.

A conventional scratch tester (REVETEST instrument made by LSRH of Switzerland) is used to study the adhesion of the films to their substrates. Diamond stylus with 200 μm tip radius is drawn across the coating surface in a stepwise increase in load moving at 10 mm/min. Adhesion test result for sample coated with a-C:H and diamond (sample (c)) is given in Figure 4. A slight wear of coating on the stylus track upon imposing a load of five newtons is clearly observed (Figure 4 (a)). However, upon increasing the load, the film starts to experience some cracking with semicircular trajectories parallel to the leading edge of the diamond stylus (Figure 4(b)-(e)). In addition, the width of the scratch track gets wider as well due to the increasing applied loads. Increasing the load to 68 newtons leads to scratch as wide as 200 μm and a significant pile up of removed materials on the edges of the track, as shown in Figure 4 (f). The observed cracks are now running almost perpendicular to the direction of the stylus track. However, there is still no apparent adhesive failure at the film substrate interface at this high applied load, implying a presence of strong interfacial chemical bond. We believe that the diamond particles play a key role in obtaining this extraordinary adhesion property. It is worthwhile to note that this value of load (68 newtons) is still well above the typical L_c values of 10-50 newtons for few microns thick of TiC or TiN coatings on steel^{14,15} and 10 newtons for diamond films on SiAlON tool inserts¹⁶.

In conclusion, diamond composite films have been deposited successfully for the first time on carbon steel and 304 stainless steel substrates using plasma assisted CVD techniques. The deposited composite films are found to be relatively flexible within 10 degrees, highly impermeable, chemically inert, and adherent. These films are superior to most carborundum, such as TiC and TiN, and can provide a good flexible protective layer on various materials.

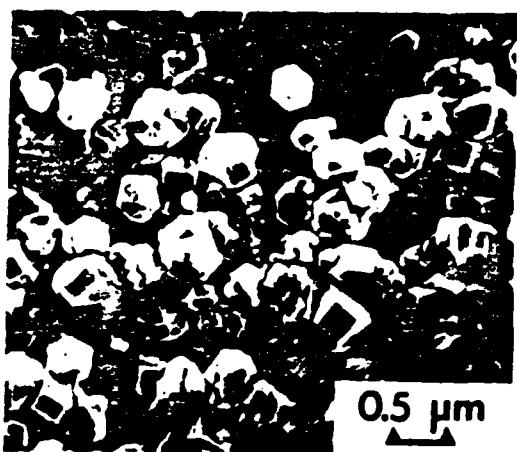
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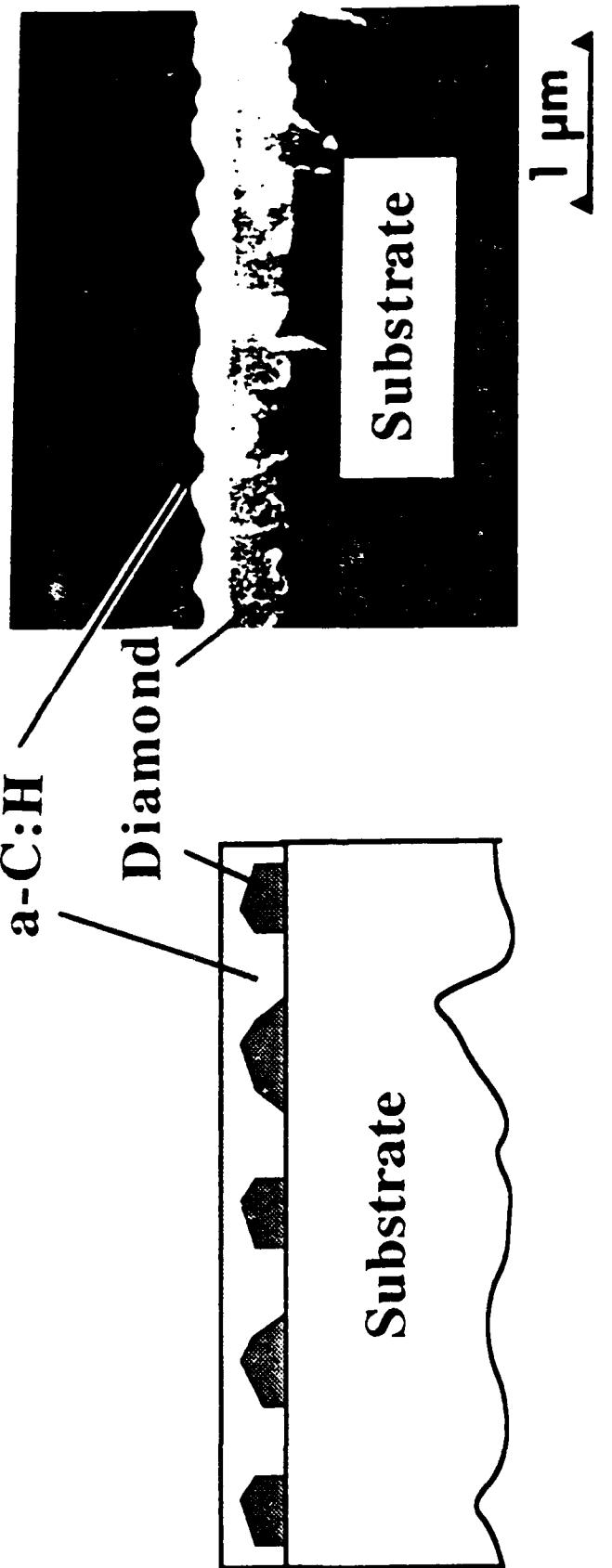
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TABLE I. Typical deposition conditions for a-C:H and fluorocarbon films.

Film	CH ₄ (sccm)	Ar (sccm)	CF ₄ (sccm)	P (mTorr)	Power (W)
a-C:H	100	25	----	10	15
Fluorocarbon	15	----	75	30-40	< 5





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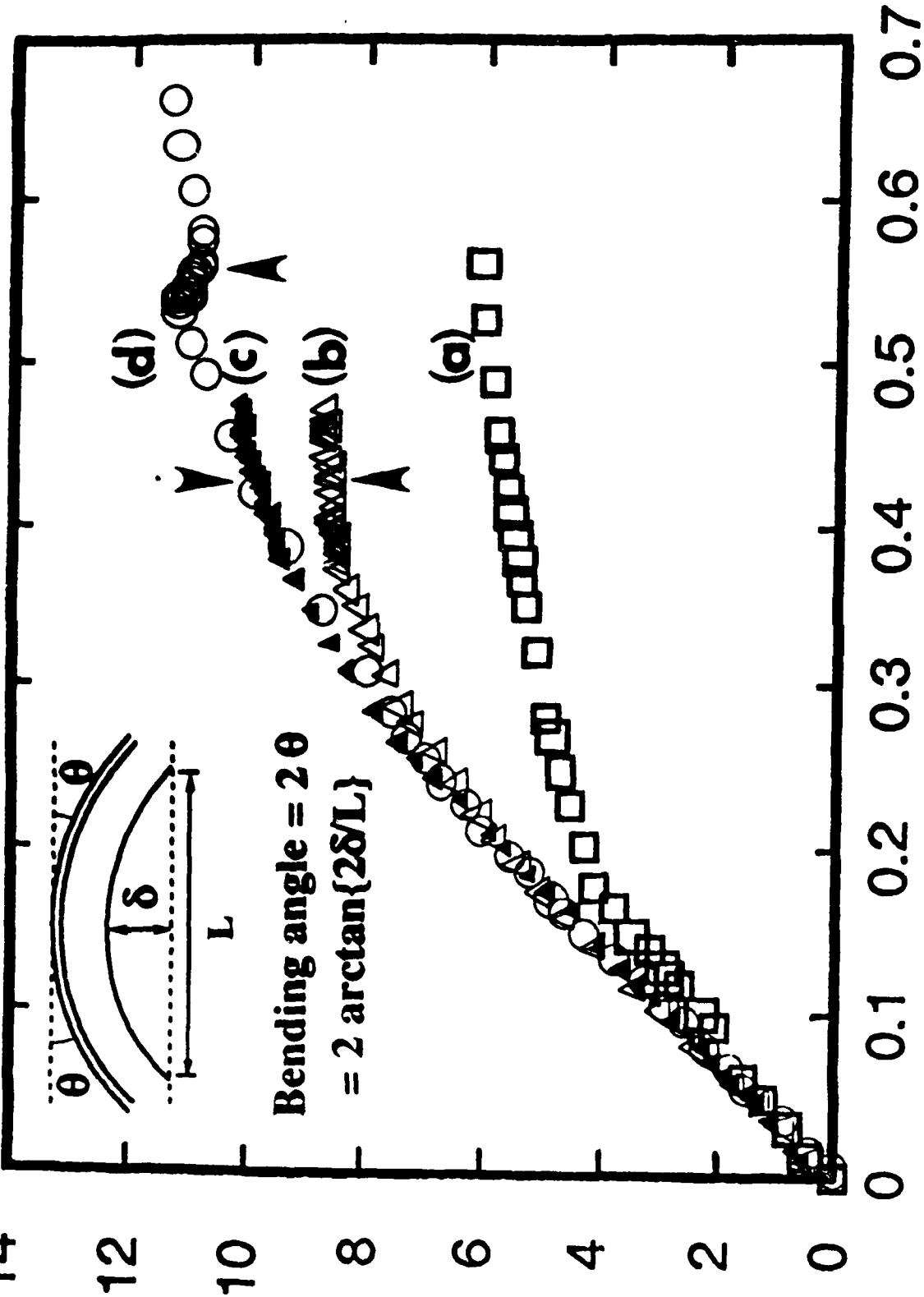
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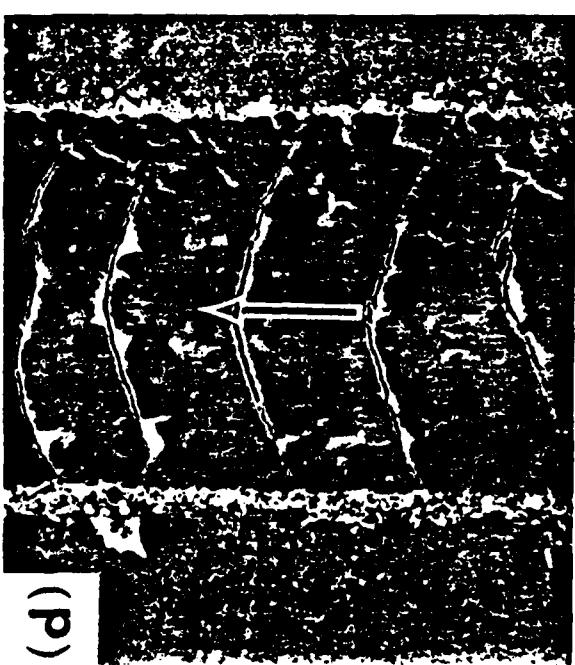
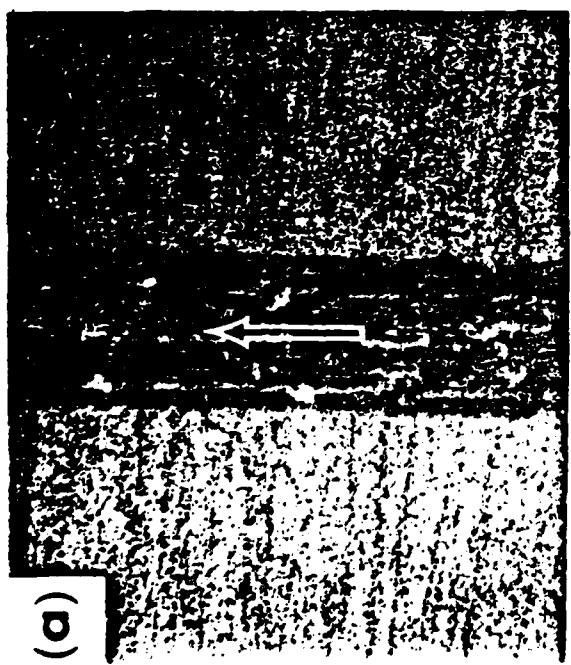
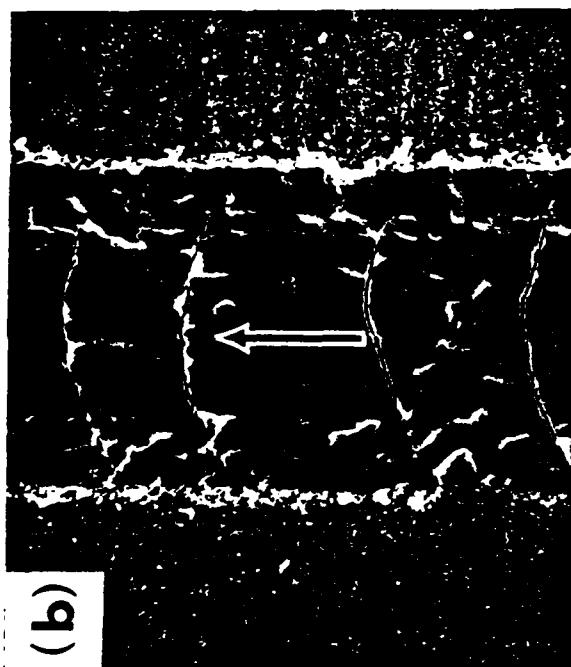
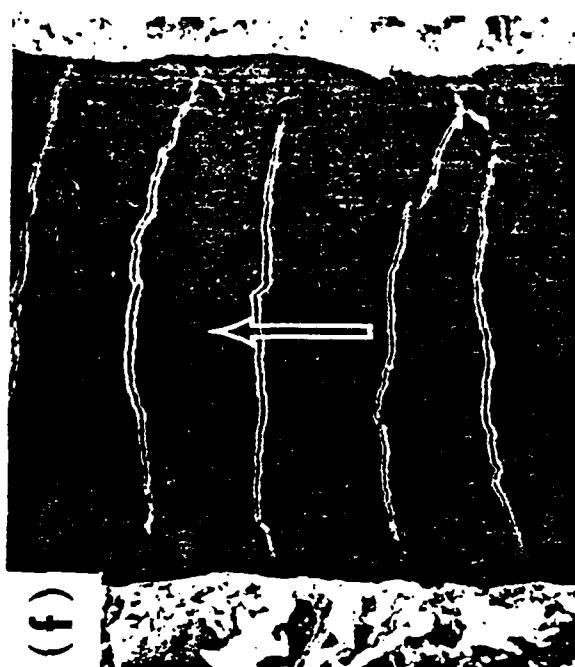
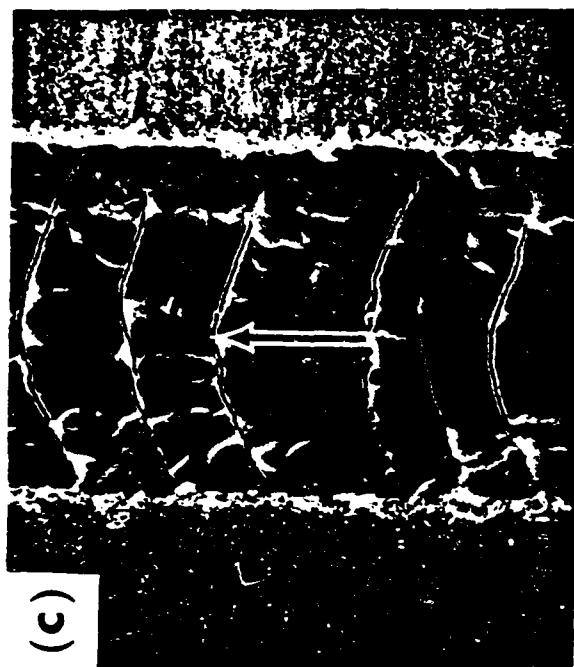
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Load/bh³ (10⁻⁶ lbf/in.⁴)

Displacement (mm)





100 μm

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